Conference Paper

Orientation Dependence of the Thermal Expansion Coefficients of Iron Borate $FeBo_3$ Crystals

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Abstract

We present high-resolution X-ray diffraction measurements of the lattice parameters of iron borate $FeBO_3$. These measurements were performed at room temperature and at various temperatures ranging from 400 up to 600°C, enabling the determination of the coefficients of thermal expansion (CTE). The three-dimensional (3D) indicatory surface of thermal expansion of $FeBO_3$was constructed in MathCad. It is shown that the orientation dependence of CTE in $FeBO_3$ is spheroid elongated on threefold axis.

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1. Introduction

$A^{III}BO_3$ (where A – Fe, Al, In, Ti, Sc, V, Cr, Yb) metal orthoborates have been known for many years to be isostructural wits calcium carbonate, $CaCO_3$[1].

Particularly interesting is iron borate $FeBO_3$, which is a weak antiferromagnet at ambient conditions. The combination of optical transparency in the visible spectral range with spontaneous magnetization at room temperature allows use of $FeBO_3$in magnetooptical devices[2].

The functional characteristics of iron borate are dependent on temperature: there are changes in the phase composition of the samples, in the structural characteristics of the crystal lattice, in crystallite size, etc. For example, in $FeBO_3$, heated to temperatures of about 700-800°C there are new phases: hematite Fe_2O_3 and $Fe_3BO_6$with norbergite structure[3].

Since, there are no data on the thermal expansion coefficients of iron borate$FeBO_3$in the literature [4]. In this work we report the results of studying of $FeBO_3$lattice parameters by high-temperature X-ray diffraction.

2. Object and method of research

Iron borate crystallize in the calcite-type structure with space group $R\bar{3}c$. It is formally described as formed by slightly distorted [FeO_6] octahedra whose O atoms belong to different [BO_3] triangulars. [BO_3] groups present reversed orientations alternating layers; while [FeO_6] octahedral share corners with other six octahedral, three from the upper layer and three from the lower layer, Figure 1.

The space group has an R-type Bravais lattice; thus, the unit cell parameters can be specified in both primitive rhombohedral (table 1) and triple hexagonal systems.

The rhombohedral parameters of $FeBO_3$ structure: a_r=5.52 Å, α_r=49.54°, V_r= 89.532Å^3; the hexagonal parameters: a_h=4.626(1) Å, c_h=14.496(6) Å, V_h=268.596 Å^3, [3]. The rhombohedral $FeBO_3$ unit cell contain two formula units.

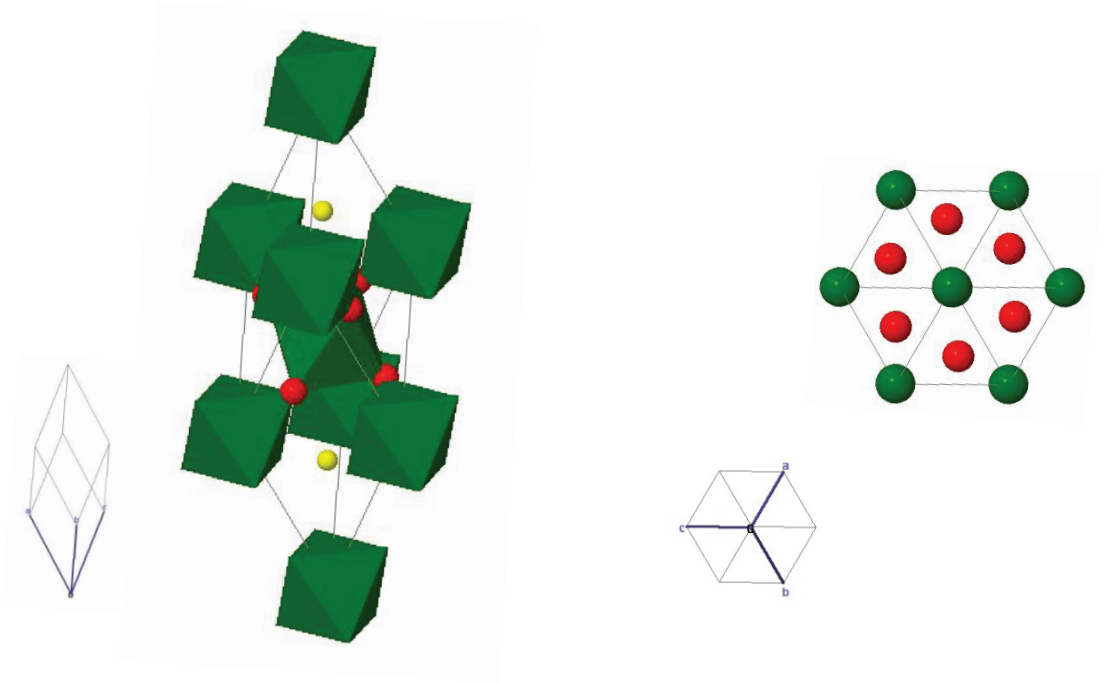

Figure 1: The primitive rhombohedral unit-cell of the $FeBO_3$. An [FeO_6] octahedron is represented in green. Fe, B and O atoms are represented in green, yellow and red spheres, respectively.

For structural studies, samples of polycrystalline iron borate were ground into powder by standard technology. The temperature behavior of $FeBO_3$ have been determined in situ on SmartLab Rigaku diffractometer (CuK_α) in the temperature range from 25°C to 600°C. The XRD investigation of $FeBO_3$ was performed in the angle range 2θ = 20°-100° in steps h(2θ) = 0.02°, Figure 2.

Table 1: Coordinates of the atoms in rhombohedral $FeBO_3$ unit-cell, were x_r=0,5481 [2].

Symmetry of the position	Atoms	Coordinates (relative units)
S_6	Fe	$0,0,0;\frac{1}{2},\frac{1}{2},\frac{1}{2};$
D_3	B	$\frac{1}{4},\frac{1}{4},\frac{1}{4};\frac{3}{4},\frac{3}{4},\frac{3}{4};$
C_2	O	$\pm\left(x_r,\frac{1}{2}-x_r,\frac{1}{4};\frac{1}{2}-x_r,\frac{1}{4},x_r;\frac{1}{4},x_r,\frac{1}{2}-x_r\right)$

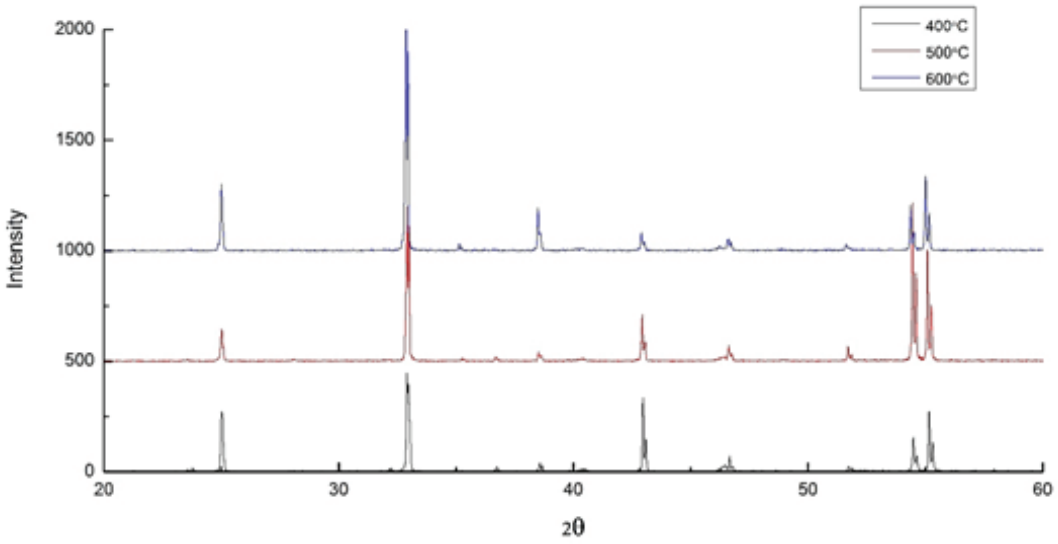

Figure 2: The X-ray powder diffraction patterns of $FeBO_3$ at 400˚C, 500˚C and 600 ˚C.

3. Analysis and discussion

The structure parameters of $FeBO_3$ were determined according to Bragg's law, [5]:

$$n\lambda = 2d\sin\theta \tag{1}$$

where n - order of diffraction,

λ - X-ray wavelength, d - interplane distance,

θ - Bragg's angle.

Indexing of diffractograms of $FeBO_3$ at the different temperatures was carried out, table 2.

The unite cell parameters of both systems calculated on the program [6] as a function of temperature are shown at table 3.

Table 2: Interference indexes of rhombohedral cell and structural characteristics d/n (Å) of $FeBO_3$ at room temperature and at 400˚C, 500˚C and 600˚C.

(h k l)	d/n (25˚C)	d/n (400˚C)	d/n (500˚C)	d/n (600˚C)
(1 1 0)	3,507	3,559	3,556	3,558
(2 1 1)	2,688	2,720	2,719	2,723
(2 2 2)	2,415	2,444	2,447	2,552
(1 0 $\bar{1}$)	2,314	2,332	2,335	2,336
(2 1 0)	2,088	2,104	2,105	2,106
(2 0 0)	1,931	1,953	1,947	1,962
(2 2 0)	1,753	1,766	1,767	1,769
(3 2 1)	1,671	1,689	1,683	1,686
(3 3 2)	1,650	1,659	1,666	1,668

Table 3: Temperature dependence of lattice constants and cell volumes of rhombohedral (r) and hexagonal (h) systems of $FeBO_3$.

	25, ˚C	400, ˚C	500, ˚C	600, ˚C
a_r, Å	5,5194±0,0003	5,5662±0,0005	5,5750±0,0004	5,5793±0,0005
α_r, Å	49,5806±0,001	49,5350±0,004	49,4570±0,001	49,4710±0,001
V_r, Å^3	89,598±0,017	91,766±0,038	91,971±0,018	92,227±0,020
a_h, Å	4,6285±0,0003	4,6620±0,0008	4,6642±0,0003	4,6691±0,0003
c_h, Å	14,4878±0,0011	14,6313±0,0011	14,6445±0,0011	14,6544±0,0014
V_h, Å^3	268,79±0,03	275,41±0,03	275,91±0,03	276,68±0,03

The dependence of the lattice constants and volume of cell on temperature has been expressed by polynoms of second order, the respective coefficients being found by the least-squares method, Figure 3.

The full fit of the data to a second-order approximation:

$$a(t) = a_0 + a_1 \cdot t + a_2 \cdot t^2 \quad (2)$$

were a_0- lattice constants at 0 ˚C,

a_1, a_2 - characteristic constants,

t - temperature in ˚C.

The values of characteristic constants determined by least-squares method are shown in table 4.

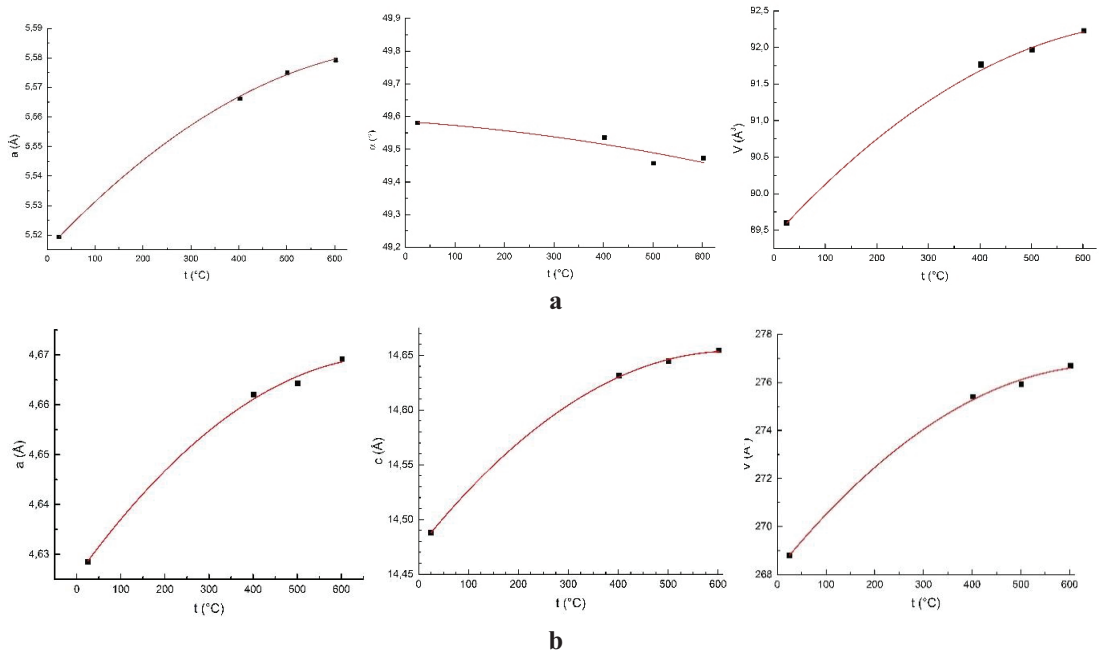

Figure 3: Temperature dependences of $FeBO_3$structure parameters: (a)rhombohedral system, (b)hexagonal system. Experimental values are shown as points (error bars are smaller than the symbols used).

Table 4: Dependence of the lattice constants and volumes V of $FeBO_3$on temperature.

Parameter	a_0	a_1	a_2
a_r, Å	5,5150	$1{,}7313\cdot10^{-4}$	$-1{,}0933\cdot10^{-7}$
α_r, °	49,5942	$-5{,}5588\cdot10^{-4}$	$5{,}7349\cdot10^{-7}$
V_r, Å^3	89,410	0,0077	$-5{,}043\cdot10^{-6}$
a_h, Å	4,6255	$1{,}2290\cdot10^{-4}$	$-8{,}5442\cdot10^{-8}$
c_h, Å	14,4740	$5{,}6931\cdot10^{-4}$	$-4{,}4978\cdot10^{-7}$
V_h, Å^3	268,189	0,0250	$-1{,}835\cdot10^{-5}$

With respect to the definition of the coefficient of the thermal expansion, [5]:

$$a = \frac{1}{a_0} \cdot \frac{da}{dt}, \tag{3}$$

were *da* – difference of lattice parameters *a* for the interval *dt*,

a_0– the lattice parameters at o°C,

dt– difference of temperature.

we obtain from (2) the dependence of thermal expansion coefficient on temperature:

$$a(t) = a_1 + a_2 \cdot t \tag{4}$$

The results of similar fits to obtain the linear thermal expansion coefficients of the two axes of the unite cell together with the resulting of volume thermal expansion, a_1 and a_2 are shown in table 5.

Table 5: Linear and volumetric thermal expansion parameters for $FeBO_3$.

Coefficients α, C^{-1}	a_1	a_2
$\alpha_{\perp z}$	$2{,}6571 \cdot 10^{-5}$	$-3{,}6943 \cdot 10^{-8}$
$\alpha_{\parallel z}$	$3{,}9333 \cdot 10^{-5}$	$-6{,}2151 \cdot 10^{-8}$
α_V	$9{,}3255 \cdot 10^{-5}$	$-1{,}3683 \cdot 10^{-7}$

Orientation dependence of the thermal expansion coefficients of the trigonal crystals described by equation [7]:

$$r = \alpha_r = \alpha_{\perp z} \sin^2\theta + \alpha_{\parallel z} cos^2\theta \quad (5)$$

where r – radius-vector,

$\alpha_{\perp z}$– CTE of perpendicular to main axis,

$\alpha_{\parallel z}$– CTE of direction along to main axis.

θ– angle of the spherical coordinate system.

The three-dimensional thermal expansion diagrams of $FeBO_3$drawing in MathCad are shown in Figure 4.

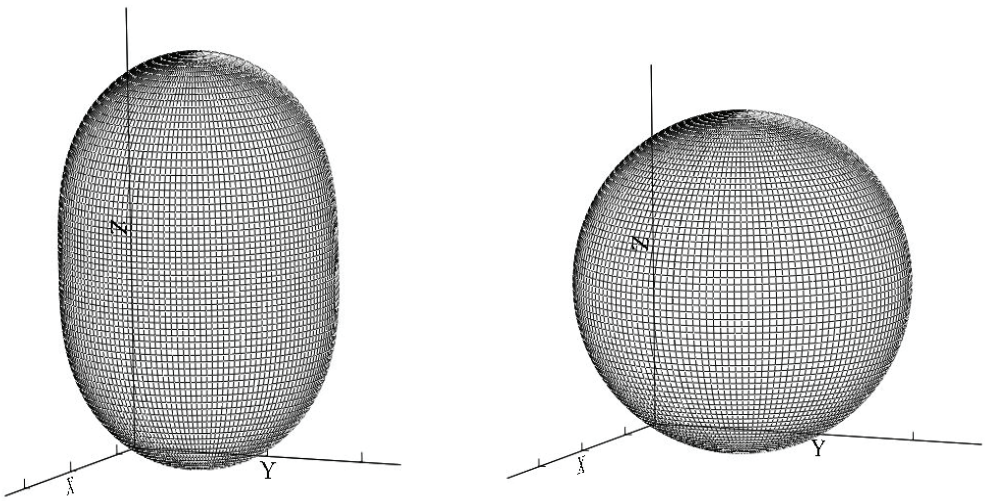

Figure 4: Indicatory surface of thermal expansion of $FeBO_3$: **a)**at room temperature ($\alpha_{\perp Z}$= 26,571·10^{-6} $C^{-1}$and $\alpha_{\parallel Z}$= 39,33·10^{-6} C^{-1}); **b)**at 400 °C – 600 °C ($\alpha_{\perp Z}$= 8,0995·10^{-6} $C^{-1}$and $\alpha_{\parallel Z}$= 8,2575·10^{-6} C^{-1}).

4. Conclusion

In this paper we report the experimental study of the thermal behavior of iron borate $FeBO_3$ by X-ray diffraction measurements and calculations. It can be seen that the thermal expansion of $FeBO_3$ is anisotropic, being greatest for the Z-axis (i.e. for the direction along the axis of the 3-order symmetry) and smallest for the direction perpendicular to the Z-axis.

In that below Neel point T_N = 75°C, $FeBO_3$ is an easy plane weak ferromagnet with the anomalous temperature variation of the thermal expansion near the phase transition temperature [4], further studies are needed in this temperature range.

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